Low energy cost conversion of methane to ethylene in a hybrid plasma-catalytic reactor system

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ABSTRACT

In this work, we report on low energy cost methane conversion to ethylene in a hybrid plasma-catalytic reactor system. Methane is first converted to acetylene, reaching up to 23.5% yield per pass, by a nanosecond pulsed discharge (NPD), and subsequently, acetylene is hydrogenated to ethylene using a Pd-based catalyst, which is placed in the post-plasma zone. Overall, ethylene is

formed as major product at 25.7% yield per pass, consuming 1642 kJ/molC₂H₄, which is the lowest energy cost reported for plasma-assisted methane-to-ethylene conversion so far. The two-step process is carried out in a single reactor volume that aside from the discharge energy does not require any heat or hydrogen input since both are provided by methane cracking in the plasma zone itself.

Keywords: methane coupling, non-thermal plasma, hybrid plasma-catalytic reactor, nanosecond pulsed discharge, ethylene

1. Introduction

Methane, the major compound in natural gas, is deemed a promising alternative feedstock for fuels and chemicals [1,2] due to its wide availability and low cost. Recent hydrocarbon explorations worldwide have revealed an abundance of conventional and unconventional rich-in-methane (CH₄) gas reserves such as tight gas, shale gas, methane hydrate and coalbed methane [3-6]. However, about half of the natural gas reserves are located in remote areas, far away from any sizeable market [7,8]. Those decentralized gas reserves have low commercial interest due to costly transportation, unless they can efficiently be converted to added value products on site.

CH₄ can be converted into added value products either in two steps, via synthesis gas [9], or directly to C₂ hydrocarbons in one step. Pyrolysis [10,11], partial oxidation [12,13], dry [14,15] and steam reforming [16] constitute CH₄ valorization processes of great commercial interest [17]. Non-oxidative CH₄ coupling has also attracted attention [18] since the formed C₂ hydrocarbons have high market value. In view of ethylene (C₂H₄) and acetylene (C₂H₂) production from CH₄, various catalysts have been studied. Recently, Guo et al. synthesized an iron-based catalyst

(Fe/SiO₂) that enables direct non-oxidative CH₄ coupling at 1363 K with 23.4% ethylene yield [19]. However, the high energy demand due to the high pyrolysis temperatures (>1100 °C) and the shortcomings associated with the pyrolytic furnaces, such as long start-up/shut-down periods, high volumetric footprints and gas emissions, are considered as important process limitations [20,21].

Plasma-assisted CH₄ cracking and particularly non-thermal plasma (NTP) may be a promising alternative solution [22-25]. High energy electrons created in the plasma zone can effectively generate a high concentration of chemically active species such as radicals, excited species and ions through electron-molecule collisions. The generated active species can rapidly undergo several chemical reactions [25] at atmospheric pressure and low temperatures. Low reaction volumes are needed due to the fast electron-induced reactions. The technology is also compatible with the renewable energy sources, which electricity may be drawn from, leading to gas emissions elimination. Undesirably, plasma is not selective and results in wide product distribution. C₂ yields strongly depend on the discharge energy density. High energy density discharges (i.e. microwave, gliding arc, spark and corona) reach up to 71% CH₄ conversion at 1861 kJ/mol_{CH₄} energy input [26]. C₂H₂ is the dominant product (60.3% selectivity), while C₂H₄ is formed in small amounts (6.3% selectivity) [26]. Low energy density discharges (i.e. DBD) reach up to 7.5% CH₄ conversion at 482 kJ/mol_{CH₄} energy input [26]. Ethane (C₂H₆) is the dominant product (42.9% selectivity), while C₂H₄ selectivity is significantly lower, 2.4% [26]. The product distribution variation observed among the different plasma sources is due to different plasma characteristics that drive the plasma chemistry.

Nanosecond pulsed discharges (NPD) show higher energy efficiency than other plasma sources [27]. By applying electrical pulses of high voltage rise rate (in the order of kV ns⁻¹) and short duration (tens of ns [28]), the electrical energy is channeled into the electrons, promoting electron-

induced chemical reactions. Transition to arc regime is prevented and NTP is sustained at these conditions. Collectively, electrical energy is predominantly channeled into chemical energy rather than into gas heating. Recent studies using NPD in CH₄ reforming have reported 23.5% [29] - 50% [30] CH₄ conversion, at 73 kJ/mol_{CH₄} - 250 kJ/mol_{CH₄} energy input. In all studies, C₂H₂ is formed as dominant product at 72% [30] - 85% [29] selectivity while C₂H₄ selectivity is limited, about 2% [30] - 4% [29], as in other high energy density plasmas.

Formation of C₂H₄ in the plasma zone can be enhanced via enrichment of CH₂ radicals which serve as C₂H₄ precursors. Although the reduced electric field increase may benefit CH₂ radicals formation by shifting the CH₄ fragmentation pattern from CH₃ to CH₂ [31], CH₂ cannot be the dominant species since the energetic thresholds of the electron-induced CH₄ to CH₃, CH₂, CH and C cracking reactions are close [25] and inevitably, all CH_x radicals are contemporarily present. Therefore, no significant C₂H₄ yields in plasma-driven processes have been reported so far and so, direct CH₄ coupling to C₂H₄ in plasma is still a challenge. However, C₂H₄ can be formed indirectly; C₂H₂, which is majorly formed in the plasma zone, can be catalytically hydrogenated to C₂H₄ beyond the plasma zone; the H₂ required for C₂H₂ hydrogenation is produced by CH₄ cracking in the plasma zone. Gordon et al. [32] introduced a Ag-Pd-Y zeolite catalyst in a DC plasma reactor, equipped with an external heating/cooling system to precisely maintain the reactor temperature at values suitable for catalyst operation. A global C₂H₄ yield of 19.3% was reported. Kado et al. [33] placed a Lindlar catalyst between the electrodes of a DC plasma reactor and achieved 47% global C₂H₄ yield. However, they questioned the economic feasibility of the process due to the extremely high energy consumption. Wang et al. [34] employed two reactors, an AC plasma reactor and a catalytic one to first couple CH₄ to C₂H₂ and then hydrogenate, in a second step, C₂H₂ to C₂H₄. They reported 52.1% global C₂H₄ yield. Working the same way, Wang and Guan [35] optimized

this system further by introducing recycle streams and reached 55% global C_2H_4 yield. In these works, the significantly high energy cost of C_2H_4 production was the major disadvantage of the process.

In the current work, a hybrid plasma-catalytic reactor system is proposed for low energy cost C_2H_4 production. An NPD reactor is first optimized with respect to feed flowrate, feed composition and discharge gap in order for C_2H_2 production at minimum energy cost. Then, integration of plasma with highly selective hydrogenation catalysts, placed individually in the post plasma zone, is carried out and optimized. Specifically, three hydrogenation catalysts, all supplied by Johnson Matthey (JM), were tested; a commercial palladium (Pd)-based catalyst, a Pd/ Al_2O_3 catalyst and a Au/ TiO_2 catalyst. The two-step process takes place in the same reactor volume while neither extra source of hydrogen, nor heat, are required; both are provided by CH_4 cracking in the plasma zone. The global C_2H_4 yield of this self-sustained hybrid plasma-catalytic reactor system reaches 25.7% at significantly lower energy cost, 1642 kJ/mol C_2H_4 , compared to previous works.

2. Material and Methods

2.1 Experimental setup

The experimental setup used for the experiments performance is presented in Figure 1. The discharge was initiated by a nanosecond pulsed power supply (n-PS) (NPG-24/2500, Megaimpulse Ltd.) which was triggered by a waveform generator (WFG) (33220A, Keysight Technology) at frequencies up to 3 kHz. A high-voltage probe (P6015A, Tektronix) and an I/V converter (CT-D-1.0, Magnelab) were employed to measure the applied voltage and discharge current, respectively, which were recorded over the course of the experiment by a digital oscilloscope (Wavesurfer 10, Teledyne Lecroy) with a sampling frequency of 10 GS/s. The discharge energy input was estimated

as in other work [36]. The integral of the instantaneous power ($V \times I$), corrected by the voltage (V) and current (I) signals time delay, constitutes the pulse energy. Voltage and current signals time delay was calculated by zeroing the $V \times I$ product time integral under absence of discharge, managed by filling the plasma reactor with SF_6 [37].

Figure 1. Experimental setup scheme: MFC, mass flow controllers; PFC, pressure flow controller; WFG, waveform generator; n-PS, nanosecond pulsed generator; co-axial plasma reactor; HPV, high voltage probe; OSCILLOSC, oscilloscope; GC-TCD, gas chromatography with thermal conductivity detector.

Mass flow controllers (GF40 Series, Brooks Instrument) controlled the feed flowrate of the reactants (CH_4 , Airliquide 99.995 % purity, and H_2 , Airliquide 99.999 % purity). A filter (SS-4TF-7, Swagelok) with 7-micron pore size was installed at the plasma reactor outflow to retain the formed carbon. A differential pressure meter (Model 700.02, WIKA) was used to monitor the differential pressure across the filter cloth, which was cleaned when the differential pressure

exceeded a certain value. A second clean identical filter was used while the first one was under cleaning. A third mass flow controller (GF40 Series, Brooks Instrument), which was operated as flowmeter, continuously recorded the volumetric flowrate of the plasma reactor outflow. However, the readout value depends on a gas factor, which varied with the gas composition. Since the gas composition was not constant over the course of the plasma reaction, N₂ (Airliquide, 99.999 % purity) was used as internal standard to accurately measure the value of the volume of the plasma reactor outflow. A known amount of N₂ (20 sccm) was fed into the plasma reactor outflow (not inside the plasma zone) [38]. The outflow rate was obtained by multiplying the initial total flowrate (CH₄ + H₂ + N₂) by the ratio of the chromatographic area of N₂ before and during the discharge. A fourth mass flow controller (4800 series, Brooks Instrument) was used to set the internal standard N₂ flow. Pressure probes (P1600 and P1650, Pace Scientific) and thermocouples (PT 900 Pace scientific) were employed to monitor the reactor operating conditions.

The analysis of the plasma reactor product stream was performed by an on-line GC (3000 MicroGC, Inficon). Detection of H₂, N₂ and CH₄ was done by a molesieve column (10 m) with backflush (3 m, Plot U); detection of C₂H₄, C₂H₆, C₂H₂, C₃H₈, C₃H₆ and C₃H₄ was done by a Plot U column (10 m) with backflush (1 m, Plot Q), while an Alumina column (10 m, 0.32 mm) with backflush (1 m, 0.32 mm, Alumina) was used for detection of higher species, i.e. C₄-C₆ hydrocarbons.

The nanosecond pulsed (co-axial) plasma reactor is presented in Figure 1. Minor adaptations to the plasma reactor, which regard the outer (ground) electrode diameter, were carried out to enable the investigation of the discharge gap impact on CH₄ conversion and product distribution. The following four tubes with different internal (ID) and external (OD) diameters were used: 7 mm ID, 10 mm OD; 10.4 mm ID, 13 mm OD; 12.2 mm ID, 18 mm OD and 22.4 mm ID, 25.4 mm OD,

which correspond to 2.4 mm, 4.2 mm, 6 mm and 10.1 mm discharge gap, respectively. The length of the outer electrode was constant (25 cm) in all tested gaps.

2.2 Catalyst preparation and utilization

To maximize the global C_2H_4 yield, three different hydrogenation catalysts were tested individually in the post-plasma zone. One commercial and one “for-research-purpose” Pd-based catalyst, both supplied by Johnson Matthey (JM) (Pd load < 0.1% w/w), were selected due to the Pd superior hydrogenation ability and its common use in industrial hydrogenation processes. Hereafter, the first (commercial) catalyst will be referred to as Johnson Matthey-developed Pd-based catalyst (JM catalyst) and the second one simply as Pd/Al₂O₃ catalyst. The latter catalyst in particular consisted of Pd (0.05% w/w) impregnated into α -alumina (Pd/Al₂O₃). This catalyst was prepared according to the following procedure; Pd(NO₃)₂ was added to alumina powder and mixed thoroughly; the mixture was dried at 120°C and calcined at 300°C to promote conversion of Pd(NO₃)₂ into PdO. Subsequently, it was compressed, crashed and sieved, resulting in granulates of 0.85 - 1.4 mm size. The third catalyst, also prepared by JM, consisted of Au (1% w/w) impregnated into titanium dioxide and is further referred to as Au/TiO₂ catalyst.

The plasma-catalyst integration was studied in the same experimental setup. All three hydrogenation catalysts were placed inside the co-axial plasma reactor, right beyond the plasma zone (post plasma zone). Therefore, neither extra heat source, nor an additional reactor, was used to perform the hydrogenation reaction. To ensure that sufficiently high temperature for the hydrogenation reaction (>200 °C) was maintained up to the point where the catalyst was placed, the ground electrode was thermally insulated. A layer of glass wool, covered by cylindrical ceramic elements (thickness of 3.5 mm) and an additional outer mantel, made of aluminum foil and glass

wool, constituted the thermal insulation. The hybrid plasma-catalytic reactor schematic is presented in Figure 2. The post plasma zone, where the hydrogenation catalyst was placed, the way the catalyst was placed, and the thermal insulation layers are also presented in Figure 2. The outer reactor wall temperature, in the zone where the catalyst was placed, was measured by a thermocouple $\sim 300\text{ }^{\circ}\text{C}$, that is sufficiently high for the hydrogenation reaction.

Figure 2. Hybrid plasma-catalytic reactor system; left: schematic of the post plasma zone - hydrogenation catalyst position; middle: representation of the catalyst placement inside the co-axial plasma reactor; right: the ground electrode of the plasma reactor with the layers of the thermal insulation.

Prior to the study of methane-to-ethylene conversion in the hybrid plasma-catalytic reactor, the catalysts were pretreated according to the supplier's indication: Pd catalysts (both commercial JM catalyst and $\text{Pd}/\text{Al}_2\text{O}_3$) were reduced in H_2 environment in the temperature range $350 \pm 30\text{ }^{\circ}\text{C}$ for one hour. To that end, the discharge was ignited in H_2 presence, at about 17 kV, 100 sccm H_2 and 3 kHz, serving as heat source. Although reduction was not required for Au/TiO_2 , the catalyst was

pretreated under the same conditions as the Pd catalysts except for shorter period (30 minutes) to remove the moisture.

2.3 Reactor performance evaluation

The impact of the tested parameters on CH₄ conversion and product distribution was evaluated based on the plasma reactor outlet stream product composition and the energy consumption over the course of the experiments. The following quantities were employed to evaluate the impact of the tested parameters on the plasma reactor performance: CH₄ conversion and H₂ and C₂ species selectivity. These quantities were defined as

$$CH_4 \text{ Conversion } [\%] = \left(1 - \frac{[CH_4]' \times v'}{[CH_4]^0 \times v^0} \right) \times 100 \quad (1)$$

$$H_2 \text{ Selectivity } [\%] = \left(\frac{1}{2} \times \frac{[H_2]' \times v' - [H_2]^0 \times v^0}{[CH_4]^0 \times v^0 - [CH_4]' \times v'} \right) \times 100 \quad (2)$$

$$C_2H_x \text{ Selectivity } [\%] = \left(\frac{2 \times [C_2H_x]' \times v'}{[CH_4]^0 \times v^0 - [CH_4]' \times v'} \right) \times 100 \quad (3)$$

$$C_2H_x \text{ Yield } [\%] = \frac{CH_4 \text{ Conversion } [\%] \times C_2H_x \text{ Selectivity } [\%]}{100} \quad (4)$$

where [...] ⁰ and [...] ' are the concentrations of CH₄ at the plasma reactor inlet and outlet stream, respectively, obtained by the on-line GC analysis; v and v' are the respective volumetric flowrates after the correction.

As energy consumption minimization for C₂H₄ production was a key objective in this work, the energy cost (EC) was employed as suitable quantity to facilitate comparison among the different published works. EC expresses the total amount of energy consumed in the hybrid plasma-catalytic reactor to produce a mole of C₂H₄. The formula of EC is given below:

$$EC \left[\frac{kJ}{mol_{C_2H_4}} \right] = \left(\frac{2 \times 60 \left[\frac{s}{min} \right] \times 22.414 \left[\frac{mL}{mol} \right] \times E_{pulse} \left[\frac{J}{pulse} \right] \times f \left[\frac{pulses}{s} \right]}{flow_{CH_4} \left[\frac{mL}{min} \right] \times Yield_{C_2H_4} [\%]} \right) \quad (5)$$

The pulse energy was calculated as in other works [36,39].

This formula (5) was also employed for the calculation of the C₂H₂ energy cost, presented in section 3.1, using, however, the respective C₂H₂ yield, instead of the C₂H₄ yield. The quantities (1), (2), (3), (4) and (5) were used for the performance evaluation of both the plasma-alone and the hybrid plasma-catalytic reactor configuration.

3. Results and Discussion

The characteristics (electron energy and electron density) of the NPD, initiated in the co-axial plasma reactor, and the plasma reactor performance (CH₄ conversion, C₂ selectivity and energy consumption) are affected by the feed flowrate and composition. Geometry aspects, such as the inter-electrode gap (discharge gap), also affect the nature of the plasma and, consequently, CH₄ conversion and C₂ selectivity. Herein, we investigate the impact of each aforementioned parameter on CH₄ conversion, C₂ selectivity and energy consumption; only the tested parameter is varied keeping the other parameters constant.

3.1 Optimization of the plasma-assisted CH₄ coupling to C₂H₂

3.1.1 Flow rate

The effect of flowrate on the plasma reactor performance is investigated by varying the feed (pure CH₄) flowrate in the range 100-800 sccm at constant applied voltage (~17 kV), frequency of 3 kHz and a discharge gap of 2.4 mm. The supplied energy is constant (0.0044 ± 0.0001 J/pulse) and independent on the feed flowrate, as shown in Table 1 (Energy; J/pulse). The experimental

conditions are identical for all the tested flowrates and so, a similar number of high energy electrons with similar electron energy are expected to be generated in the plasma zone. The specific energy input (SEI; kJ/mol_{CH₄}) decreases when increasing the feed flowrate, but the CH₄ dissociation rate increases (Table 1; dissociation rate; cracked mol_{CH₄}/s) as more CH₄ molecules pass through the plasma zone per unit of time and the collision frequency between electrons and CH₄ molecules increases. Moreover, the higher the CH₄ molecule flux, the shorter the time a CH₄ molecule remains in the plasma zone and thus, the lower the number of discharges a molecule may experience, as presented in Table 1 (no. of discharges; pulses/ molecule_{CH₄}) using Equation 6.

$$N_{pulses} = \frac{d_p}{\frac{Q}{A} \left[\frac{m^3 \cdot s^{-1}}{m^2} \right]} \times f \left[\frac{pulses}{s} \right] \quad (6)$$

In the above relation, d_p represents the plasma streamer diameter and is considered equal to 0.3 mm, as has been estimated elsewhere [30] for nanosecond pulsed discharges. Q represents the volumetric feed flowrate. A is the cross section area of the tubular reactor and f is the pulse repetition frequency.

The fact that a CH₄ molecule may experience less discharges leads to a lower probability an already cracked CH₄ molecule (CH₃, CH₂ or CH) to recollide with another electron; consequently, more efficient utilization of the generated electrons is promoted since the electrons are used to crack new CH₄ molecules instead of radicals which were formed by the already cracked CH₄ molecules. This is also confirmed by the reduction of the C₂H₂ energy production cost (Figure 3).

Table 1. The effect of feed flowrate variation on the pulse energy, specific energy input, CH₄ dissociation rate and maximum number of discharges a molecule may experience at constant applied voltage, frequency of 3 kHz and discharge gap of 2.4 mm.

Flow rate [sccm]	Energy [J/pulse]	SEI [kJ/mol _{CH₄}]	Dissociation rate [mol _{CH₄} /s]	No. of discharges [pulses/ molecule _{CH₄}]
100	0.0044	178.6	$3.1 \cdot 10^{-5}$	18.33
200	0.0043	87.9	$3.4 \cdot 10^{-5}$	9.16
400	0.0043	43.8	$4.0 \cdot 10^{-5}$	4.58
800	0.0045	22.7	$6.0 \cdot 10^{-5}$	2.29

Although the CH₄ dissociation rate increases with feed flowrate increase from 100 to 800 sccm, CH₄ conversion decreases from 42% to 10% (Figure 3). This is due to CH₄ feed flowrate increasing at a higher rate compared to CH₄ dissociation rate, and since conversion is calculated with respect to CH₄ inflow, CH₄ conversion drops.

The dominant formed product at all tested flowrates is C₂H₂, even though the total selectivity to C₂ products changes with flowrate increase (Figure 4). Specifically, C₂H₂ selectivity decreases from 59.8% to 47.6%, while C₂H₄ and C₂H₆ selectivities increase from 7% to 11.1% and from 2.7% to 5.5%, respectively, when CH₄ feed flowrate increases from 100 to 800 sccm. This may be explained by the fact that increase in feed flowrate results in a lower number of discharges that a CH₄ molecule experiences and so, in a lower probability for an already cracked molecule (i.e. CH₃ or CH₂) to be further dissociated to CH and carbon. Consequently, the concentration of CH radicals, which constitute precursors for C₂H₂ formation, may be lower at higher flowrates, resulting in C₂H₂ selectivity drop. On the contrary, the concentrations of CH₃ and CH₂ radicals may increase, resulting in higher selectivity to C₂H₆ and C₂H₄. In addition, shorter effective residence times in the plasma zone and faster quenching rates, attained by feed flowrate increase, may prevent degradation of the formed products in secondary reactions [40]. Dehydrogenation of formed C₂H₄ and C₂H₆ to C₂H₂ (and further to carbon) may be suppressed as the temperature

abruptly drops when the hot products exit the confined plasma filament, in which temperature may reach very high temperatures (up to 3200 °C), as measured by Yao et al. in a similar configuration [29], and mix with the low-temperature unconverted gas resulting in bulk gas temperature around 300 °C. The yield of C_2H_2 decreases from 25.1% to 4.8% with feed flowrate increase from 100 sccm to 800 sccm (Figure 3), because of the simultaneous decrease in both conversion and selectivity. The yield of C_2H_4 drops from 3% to 1.1%, even though C_2H_4 selectivity increases; CH_4 conversion substantially affects the yield since it decreases almost four times.

Figure 3. The effect of feed flowrate on CH_4 conversion, C_2 products yields and C_2H_2 energy production cost at constant applied voltage, frequency of 3 kHz and discharge gap of 2.4 mm.

Figure 4. The effect of feed flowrate on C₂ products selectivities at constant applied voltage, frequency of 3 kHz and discharge gap of 2.4 mm.

3.1.2 Addition of Argon

The effect of argon addition to CH₄ feed on CH₄ conversion and C₂ selectivities is investigated. A fixed amount of Ar, 20 sccm, is added to 400 and 200 sccm of CH₄ and the plasma-assisted CH₄ coupling reaction is performed under identical conditions (constant applied voltage, frequency of 3 kHz and discharge gap of 2.4 mm). Conversion of CH₄ in presence of Ar is always higher than in the case of pure CH₄ feed, as shown in Figure 5. Conversion increases from 30.3% to 35.7% and from 16% to 17.5% when 20 sccm of Ar are added to 200 sccm (1:10) and 400 sccm (1:20) of pure CH₄, respectively.

The presence of Ar alters the CH₄ activation mechanism in the plasma zone. The metastable Ar* species, which are formed inside the discharge, act as effective energy carriers for the electron induced CH₄ dissociation reactions; energy is transferred from the excited atoms (Ar*) to the neutral CH₄ molecules via third-body reactions, promoting CH₄ dissociation. The energetic thresholds of Ar*/CH₄ dissociation reactions are lower than the respective electron-induced ones [41,42] (Table 2). Thus, the CH₄ dissociation rate increases when Ar is added at constant specific energy input (Table 3). Ar molecules excitation to Ar*(³P₂) is energy intensive (Table 2), though, and inevitably, a considerable part of the energy pulse is consumed in Ar*(³P₂) formation, at the expense of other electron-induced CH₄ cracking reactions. Therefore, CH₄ conversion does not notably increase when Ar is added at such low concentrations (Table 3). Ar addition leads to C₂ products selectivity decrease. The total C₂ selectivity drops from 65.3% to 46.5% and from 64.6% to 47.3% with 20 sccm Ar addition to 200 and 400 sccm of pure CH₄, respectively, possibly

because Ar^*/C_2 third-body reactions occur, resulting in C_2 dissociation to carbon. This is evidenced by the higher carbon accumulation (inside the reactor) that is observed when Ar is added.

Table 2. Energy thresholds of the electron-induced and third-body (Ar^*/CH_4) dissociation reactions

Electron induced reactions	Threshold energy	Third-body reactions	Threshold energy
$\text{CH}_4 + \text{e}^- \rightarrow \text{CH}_3 + \text{H} + \text{e}^-$	19 eV	$\text{CH}_4 + \text{Ar}^* \rightarrow \text{CH}_3 + \text{H} + \text{Ar}$	14.5 eV
$\text{CH}_4 + \text{e}^- \rightarrow \text{CH}_2 + \text{H}_2 + \text{e}^-$	10 eV	$\text{CH}_4 + \text{Ar}^* \rightarrow \text{CH}_2 + 2\text{H} + \text{Ar}$	19.3 eV
$\text{CH}_4 + \text{e}^- \rightarrow \text{CH} + \text{H}_2 + \text{H} + \text{e}^-$	11 eV	$\text{CH}_4 + \text{Ar}^* \rightarrow \text{CH} + \text{H}_2 + \text{H} + \text{Ar}$	19.2 eV
$\text{Ar} + \text{e}^- \rightarrow \text{Ar}^*(^3\text{P}_2) + \text{e}^-$	11.6 eV		

Table 3. The effect of Ar addition on the pulse energy, specific energy input and CH_4 dissociation rate at constant applied voltage, frequency of 3 kHz and discharge gap of 2.4 mm.

Feed flow rate [sccm]	Energy [J/pulse]	SEI [kJ/mol CH_4]	Dissociation rate [mol $_{\text{CH}_4}$ /s]
200	0.0058	120.1	$4.6 \cdot 10^{-5}$
200+20	0.0066	120.1	$5.3 \cdot 10^{-5}$
400	0.0065	67.8	$4.8 \cdot 10^{-5}$
400+20	0.0065	67.8	$5.2 \cdot 10^{-5}$

Figure 5. The effect of Ar addition on CH₄ conversion and C₂ products selectivities at constant applied voltage, frequency of 3 kHz and discharge gap of 2.4 mm.

3.1.3 Addition of H₂

Holmen and his co-workers [43] reported that hydrogen addition to the feed generally results in suppression of carbon and benzene formation and increase in acetylene selectivity, at the expense of conversion though, in methane coupling processes. Since carbon formation constitutes the major obstacle towards stable performance and long duration operating cycles, H₂ is cofed with CH₄. Based on previous works [10,44] CH₄:H₂ = 1:1 (in molar base) leads to a fair tradeoff between low carbon formation and satisfactory methane conversion. In the current work, equimolar feed of H₂ and CH₄ is tested. Although CH₄ conversion drops from 42% (Figure 3) to 34.1% (Figure 7), C₂H₂ selectivity slightly increases from 59.8% (Figure 4) to 60.3% (Figure 5) and, most importantly, the discharge stability is enhanced. Therefore, equimolar feed of H₂ and CH₄ is used in all further experiments.

3.1.4 Plasma reactor performance at different inter-electrode gaps

The gap between the high voltage and the ground electrode (Figure 6) strongly affects the applied electric field and, thus, the plasma characteristics. Consequently, the performance of the plasma reactor is affected.

Figure 6. Graphical representation of inter-electrode gap and initiation of the plasma in the reactor used for the experiments; D : ground electrode inner diameter; d_{spark} : spark streamer diameter; d : high voltage electrode diameter; Gap: discharge gap.

The effect of discharge gap on CH_4 conversion and product selectivities is investigated. Four different ground electrodes with different dimensions, which correspond to 2.4 mm, 4.2 mm, 6 mm and 10.1 mm gaps are used to test the effect of the gap. The experiments are run under constant applied voltage, frequency of 3 kHz and total feed flowrate of 200 sccm ($\text{H}_2:\text{CH}_4 = 1:1$).

Figure 7 shows that CH_4 conversion decreases from 34.1% to 21.7% with gap increase from 2.4 mm to 10.1 mm. This is because the channeled energy into the discharge is not constant for the different gaps, but, rather, decreases with increasing discharge gap. Since higher breakdown voltages are required to ignite the discharge at higher gaps [45] (more energy is spent on the plasma ignition process) and considering that the energy amount of a pulse supplied by the power supply is always constant, less energy remains to be channeled into the discharge at higher gaps. In principle, the difference between the supplied energy by the power supply and the energy required

to ignite the discharge equals the energy that is channeled into the discharge. The decrease in current (indicator of plasma energy) with the gap increase (Table 4) supports this hypothesis.

To obtain more insight into the gap effect, the reduced electric field is calculated and used as an indicator of the mean energy of electrons. The reduced electric field is given by Equation (7):

$$\frac{E}{N} [Td] = \frac{V_{app}}{d} \left[\frac{V}{\frac{cm}{cm^3}} \right] \quad (7)$$

where, E is the applied electric field and N is the number of atoms of the medium (assuming ideal gas at 1 atm, $N = 2.66 \cdot 10^{19} \text{ cm}^{-3}$); the electric field is equal to the applied voltage (V_{app}) over the discharge gap (d).

The reduced electric field is calculated based on the maximum applied voltage (E/N max) and reported in Table 4. It is shown that the reduced electric field decreases from 247 Td to 74 Td with discharge gap increase from 2.4 mm to 10.1 mm. Because of the reduced electric field decrease, electrons with lower mean energy are generated and, consequently, less effective e^-/CH_4 collisions occur. Therefore, the CH_4 dissociation rate decreases (Table 4) with gap increase, and since the CH_4 feed flowrate is constant, CH_4 conversion decreases too.

Table 4. The effect of discharge gap on the pulse energy, reduced electric field, discharge current and CH_4 dissociation rate at constant applied voltage, frequency of 3 kHz and total feed flowrate of 200 sccm ($\text{CH}_4:\text{H}_2 = 1:1$).

Gap [mm]	Energy [J/pulse]	E/N max [Td= 10^{-17} Vcm^2]	Current [A]	Dissociation rate [mol CH_4 /s]
2.4	0.0061	247	84.8	$5.1 \cdot 10^{-5}$

4.2	0.0052	171	80.1	$4.2 \cdot 10^{-5}$
6.0	0.0052	97	73.7	$3.3 \cdot 10^{-5}$
10.1	0.0043	74	48.5	$3.2 \cdot 10^{-5}$

Figure 8 shows that C_2H_2 is the dominant formed product in all tested gaps. C_2 selectivities are strongly affected by the discharge gap. C_2H_2 selectivity decreases from 60.3% to 32% with discharge gap increase from 2.4 mm to 10.1 mm. On the contrary, C_2H_4 and C_2H_6 selectivities increase from 10.4% to 20.6% and from 5% to 15%, respectively. This behavior may be attributed to the reduced electric field decrease, which could affect the CH_4 fragmentation pattern. At higher discharge gaps, less electrons with energy content higher than 11 eV may be generated, which could result in CH radicals generation and further in C_2H_2 formation. Simultaneously, more electrons with energy content of 9 eV and 10 eV may be generated, which could result in CH_3 and CH_2 radicals generation and further in C_2H_6 and C_2H_4 formation.

Overall, the yield of C_2H_2 decreases from 20.6% to 7.2% as the discharge gap increases from 2.4 mm to 10.1 mm (Figure 7) due to CH_4 conversion and selectivity decrease. The C_2H_2 yield reduction is also reflected on the C_2H_2 energy production cost which is almost doubled. The yield of C_2H_4 slightly increases from 3.5% to 4.5% since the decrease in conversion is almost balanced by the increase in selectivity.

Figure 7. The effect of discharge gap on CH₄ conversion, C₂ products yields and C₂H₂ energy production cost at constant applied voltage, frequency of 3 kHz and total feed flowrate of 200 sccm (H₂:CH₄ = 1:1).

Figure 8. The effect of discharge gap on C₂ products selectivities at constant applied voltage, frequency of 3 kHz and total feed flowrate of 200 sccm (H₂:CH₄ = 1:1).

3.2 Optimization of the hybrid plasma-catalytic CH₄ coupling to C₂H₄

Targeting low energy cost C₂H₄ production, the three JM-supplied catalysts, described in Section 2.2, namely a commercial Pd-based catalyst (JM catalyst), a Pd/Al₂O₃ catalyst and a Au/TiO₂

catalyst are individually introduced in the post-plasma zone to hydrogenate C_2H_2 to C_2H_4 at no extra energy and hydrogen supply. Both H_2 and heat, which are required for the hydrogenation reaction, are provided by the plasma zone in which CH_4 is cracked. Eventually, C_2H_2 serves as intermediate compound for C_2H_4 formation.

Since C_2H_2 serves as precursor for C_2H_4 formation in hybrid plasma-catalytic reactor systems, maximization of the global C_2H_4 yield is enabled when high C_2H_2 yield is attained in the plasma zone. Moreover, C_2H_2 to C_2H_4 hydrogenation does not add any further energy demand to the hybrid reactor system and so the C_2H_4 energy production cost is driven by the energy consumption for C_2H_2 formation in the plasma zone. Therefore, operating windows that enable high C_2H_2 yields, consuming relatively low energy, are preferable. In an industrial context, high C_2H_4 yields that can be attained in hybrid plasma-catalytic reactor systems simplify downstream separation and purification of C_2H_4 , while low energy cost boosts the economic feasibility of the process. Besides these key performance criteria, performance stability and operating cycle duration are also considered.

Although higher C_2H_2 yields and slightly lower C_2H_2 energy production costs are attained when pure CH_4 is fed, as compared to CH_4 and H_2 cofeeding, feeding pure CH_4 should be avoided as it leads to significant amount of carbon formation and eventually to discharge suppression within 15-20 minutes after discharge ignition. In the case of Ar addition, the discharge cannot operate stably either. Moreover, an additional process step for Ar reclaim would be needed at industrial scale. Operating at high flowrates, low C_2H_2 energy production costs are attained, associated, however, with low C_2H_2 yields.

After these considerations and based on the parametric study described earlier, the optimum operating window for C_2H_2 formation in the plasma zone is low applied voltage (about 17 kV),

200 sccm/ $\text{CH}_4\text{:H}_2=1\text{:}1$, frequency of 3 kHz, discharge gap of 2.4 mm and atmospheric pressure. Further optimization of the downstream catalytic step at these plasma operating conditions leads to global C_2H_4 yield maximization and C_2H_4 energy production cost minimization of the total hybrid plasma-catalytic system.

3.2.1 Hydrogenation catalyst selection

The catalytic performance of the commercial JM, $\text{Pd}/\text{Al}_2\text{O}_3$ and Au/TiO_2 catalysts were tested. The catalysts were placed in the plasma reactor, as shown in Figure 2, and pretreated as described in Section 2.2. The discharge was ignited at constant applied voltage (~ 17 kV), frequency of 3 kHz and total feed flowrate of 200 sccm ($\text{H}_2\text{:CH}_4 = 1\text{:}1$). The global C_2 and carbon (including also higher hydrocarbons) selectivities, attained in the hybrid plasma-catalytic system with the three different catalysts, are presented in Figure 9 and compared to the ones attained with the plasma-alone reactor.

Figure 9. Global C_2 products and carbon (including also higher hydrocarbons) selectivities attained in the hybrid plasma-catalytic system with use of the commercial JM, $\text{Pd}/\text{Al}_2\text{O}_3$ and Au/TiO_2 catalysts. The experiments were run at constant applied voltage of ~ 17 kV, frequency of 3 kHz, total feed flowrate of 200 sccm, $\text{H}_2\text{:CH}_4 = 1\text{:}1$ and 0.5 g of catalyst.

The JM catalyst yields the highest global C₂H₄ selectivity (63.6%); C₂H₂ and C₂H₆ selectivities are relatively low, 3.7% and 11.7%, respectively, in the hybrid plasma-catalytic system. When Pd/Al₂O₃ is used, C₂H₄ is still the major product in the hybrid plasma-catalytic system, but the global C₂H₄ selectivity (50.9%) is lower than that of the JM's catalyst. Relatively high C₂H₆ and C₂H₂ selectivities, 24.5% and 5%, respectively, are also observed in the hybrid plasma-catalytic system. In the case of Au/TiO₂, C₂H₂ is the major product (45.2% global selectivity) in the hybrid plasma-catalytic system, instead of C₂H₄ (27.1% global selectivity), indicating limited C₂H₂ hydrogenation in the catalytic step (C₂H₄ selectivity in the plasma-alone configuration is 19.9%). Pd catalysts are the most suitable catalytic materials for high global C₂H₄ yields in hybrid plasma-catalytic reactor systems. Since the objective of the current work is maximization of the C₂H₄ yield, the JM catalyst is used for further optimization.

3.2.2 Hydrogenation catalyst amount

Catalyst mass variation imposes different space velocities which may affect the catalyst performance. Herein, the impact of catalyst amount on the global C₂H₄ yield in the hybrid plasma-catalytic system is investigated. Three different amounts of JM catalyst were loaded, 0.3 g, 0.5 g and 1.0 g, which correspond to 2.75, 1.65 and 0.82 h⁻¹ weight hourly space velocity (WHSV equals the ratio of C₂H₂ amount produced in plasma-alone configuration over the amount of catalyst used for the hydrogenation) respectively, and the discharge was initiated under identical conditions (constant applied voltage of about 17 kV, frequency of 3 kHz, discharge gap of 2.4 mm and total feed flowrate of 200 sccm, H₂:CH₄ = 1:1). The global C₂ and carbon (including also higher hydrocarbons) selectivities attained in the hybrid plasma-catalytic system over the different catalyst loads, and consequently different WHSVs, are presented in Figure 10.

Figure 10. Global C₂ products and carbon (including also higher hydrocarbons) selectivities attained in the hybrid plasma-catalytic system over three different amounts of the JM catalyst: 0.3 g, 0.5 g and 1.0 g. The experiments were run at constant applied voltage of ~17 kV, frequency of 3 kHz, discharge gap of 2.4 mm and total feed flowrate of 200 sccm, H₂:CH₄ = 1:1.

In the case of 0.3 g catalyst load, C₂H₂ and C₂H₄ are produced at similar selectivities, 38.5% and 32.7% respectively, in the hybrid plasma-catalytic system. The reactants/catalyst contact time (2.75 h⁻¹) is too short to efficiently enable C₂H₂ to C₂H₄ hydrogenation. However, at higher contact times (1.65 and 0.82 h⁻¹) attained by higher catalyst loads (0.5 and 1.0 g), significant enhancement in C₂H₂ to C₂H₄ hydrogenation performance is observed. C₂H₄ is produced as major product with 67-72% global selectivity, while negligible amount of C₂H₂ remains unconverted (3.5-4.5%) in the hybrid plasma-catalytic system. No significant differences in global C₂ and carbon (including also higher hydrocarbons) selectivities between 0.5 g and 1.0 g of catalyst use are observed after the analysis error consideration; therefore, 0.5 g of catalyst is used in all experiments. More than 1.0 g of catalyst has not been used since further increase in reactants/catalyst contact time may result in C₂H₂ hydrogenation to C₂H₆ rather than C₂H₄.

3.2.3 Stability of the hybrid plasma-catalytic reactor

Besides high C_2H_4 yield and low C_2H_4 energy production cost, stable process performance is also important. Other hybrid plasma-catalytic systems reported in the literature suffered from performance instabilities. Discharge interruptions and catalyst clogging caused by carbon formation are the main reasons of unstable performance. Addition of O_2 [32], or use of a sequence of reactors [34,35], a plasma and a catalytic one, have been proposed as solutions at the expense of increasing energy consumption, as the catalytic reactor requires additional energy to reach temperatures suitable for the hydrogenation reaction. From an industrial perspective, reactor cascades would increase the capital investment while pure O_2 would be an additional expensive utility.

In this work, the proposed hybrid plasma-catalytic reactor comprises a single piece of equipment without any heating/cooling system. No additional chemical agents are required; the amount of H_2 that is cofed with CH_4 in the reactor inlet (prior to plasma processing) is less than the H_2 produced in the plasma zone. In fact, the produced H_2 exceeds the sum of H_2 amounts for a) C_2H_2 hydrogenation in the post-plasma zone and b) recycling to the reactor inlet to meet the targeted composition of $CH_4:H_2=1:1$. Although H_2 cofeeding mitigates (does not completely eliminate) carbon formation, the discharge is eventually suppressed due to formation of conductive carbon filaments, which act as short circuits. However, no discharge interruptions were noticed during the experiments. Figure 11 shows the performance evolution and fluctuation of the proposed hybrid plasma-catalytic reactor system for the case of 2.4 mm discharge gap (other conditions: JM catalyst (0.5g), constant applied voltage of about 17 kV, frequency 3 kHz and total feed flowrate 200 sccm at $H_2:CH_4 = 1:1$).

Figure 11. Performance evolution and fluctuation of the proposed hybrid plasma-catalytic reactor system when using the JM catalyst (0.5g) at constant applied voltage of about 17 kV, frequency of 3 kHz, discharge gap of 2.4 mm and total feed flowrate of 200 sccm at H₂:CH₄ = 1:1.

This operating cycle (about 1 h in Figure 11), which is rather short for industrial standards, is prolonged when larger discharge gaps are chosen, as it takes longer for the conductive carbon filaments to be formed and bridge the high voltage electrode with the ground one, eventually leading to short circuit formation and discharge suppression. However, Figure 12 shows that increase in the gap size at constant power input results in lower global C₂H₄ yield in the hybrid plasma-catalytic system, mainly due to methane conversion decrease (black line). Ultimately, use of customized solids removal equipment (e.g. cyclone and filters) between the plasma and catalytic zones would be needed at larger scales to enable long reactor runs.

Figure 12. Highest CH_4 conversion and global C_2 products and carbon (including also higher hydrocarbons) selectivities attained in plasma-alone configuration, at 2.4 and 4.2 mm discharge gaps, and hybrid plasma-catalytic system, at 2.4 and 4.2 mm discharge gaps, with 0.5 g of JM catalyst. The experiments were run at constant applied voltage of ~ 17 kV, frequency of 3 kHz and total feed flowrate of 200 sccm at $H_2:CH_4 = 1:1$.

3.3 Evaluation of the hybrid plasma-catalytic reactor performance

Only few papers on hybrid plasma-catalytic reactor systems for C_2H_4 production from CH_4 are found in the literature. These are reported in Table 5. Energy consumption is the most severe process limitation, while integration of plasma and catalyst in the same reactor volume was not possible, due to carbon formation, except for Kado et al. [33]. Although high C_2H_4 yields were reported in [33], the authors questioned the economic feasibility of their process. The hybrid plasma-catalytic reactor and the specific operating window presented in this work enable a two-step methane-to-ethylene process featuring up to 25.7% C_2H_4 yield (while commercial viability requires ethylene yields $> 25\%$ [46]) and energy cost for C_2H_4 production as low as 1642 kJ/mol. Short operating cycles, which is a significant process limitation, may be tackled by integrating solids removal equipment (i.e. cyclones and filters) with the hybrid plasma-catalytic reactor avoiding carbon deposition and eventually discharge suppression.

Table 5. Comparison with other plasma and catalytic reactor systems

Work	C ₂ H ₄ Yield [%]	Energy cost [kJ/molC ₂ H ₄]	Setup
Gordon et al. [32]	19.3	8442 + Hydrogenation	DC plasma reactor + heating/cooling system
Kado et al. [33]	47.0	not available	DC plasma reactor
Wang et al. [34]	52.1	3302 + Hydrogenation (120°C)	AC plasma + catalytic reactor
Wang and Guan [35]	55.0	3266 + Hydrogenation (150°C)	AC Plasma + catalytic reactor
<i>Current</i>	<i>25.7</i>	<i>1642</i>	<i>Hybrid reactor (one piece)</i>

4. Conclusions

Two-step methane-to-ethylene conversion has been realized in a hybrid plasma-catalytic reactor, producing high C₂H₄ yield (25.7%) at low energy cost (1642 kJ/molC₂H₄). CH₄ is activated by non-thermal plasma, generated by a nanosecond pulsed power supply, and coupled to C₂H₂ in the first step. C₂H₂ is catalytically hydrogenated to C₂H₄ by a Johnson Matthey-developed palladium (Pd)-based catalyst (JM catalyst), after the plasma zone, in the second step. Ideal thermal and chemical integration is achieved, since the gas temperature after the plasma zone is at the level required for the hydrogenation reaction (thermal integration), and the H₂ required for the hydrogenation reaction is produced from CH₄ cracking in the plasma zone (chemical integration).

High C₂H₄ yield at the end of the two-step process necessitates maximization of the C₂H₂ yield in the plasma zone itself (first step). C₂H₂ formation is driven by the plasma characteristics

(electron energy and electron density), which are strongly affected by the feed flowrate, feed composition (H_2 or Ar addition) and inter-electrode gap (discharge gap). At feed flowrates ≥ 400 sccm, low C_2H_2 energy cost (≤ 1200 kJ/mol $_{\text{C}_2\text{H}_2}$) is attained at the expense of low C_2H_2 yield ($\leq 7.5\%$). Feed flowrates ≤ 100 sccm result in high C_2H_2 yields (28.2%), but severe discharge interruptions occur due to carbon formation. When operating at moderate flowrates (100 sccm), a fair trade-off is maintained between high C_2H_2 yield ($\sim 25\%$) and low energy cost (~ 1400 kJ/mol $_{\text{C}_2\text{H}_2}$). Pure CH_4 feed should be avoided as it leads to significant carbon formation. Addition of non-hydrocarbon gases may improve the plasma performance. For example, addition of Ar, which acts as effective energy carrier, at concentrations $\geq 10\%$ v/v, results in C_2H_2 yield increase. Lower concentrations do not improve the performance. Addition of H_2 mitigates carbon formation, thereby enhancing discharge stability. Small discharge gaps at a given power supply are preferred as the reduced electric field is maximized resulting in high CH_4 conversion and C_2H_2 yield. In this work, focusing on a hybrid two-step plasma catalytic process, operating at low applied voltage (~ 17 kV), frequency of 3 kHz, discharge gap of 2.4 mm and total feed flowrate of 200 sccm ($\text{H}_2:\text{CH}_4 = 1:1$), 20.1% of C_2H_2 yield at 2200 kJ/mol $_{\text{C}_2\text{H}_2}$ energy cost was attained, as optimum performance in the first step. Pd catalysts are suitable for efficient conversion of C_2H_2 to C_2H_4 in the second step (downstream of the plasma zone). Use of the Pd-based JM catalyst resulted in the highest C_2H_4 yields (22-26%) in the WHSV range 1.65 – 0.82 h $^{-1}$.

Carbon formation, which eventually leads to discharge suppression, is a disadvantage of such hybrid plasma-catalytic systems. The remedy, especially at larger scales, will be the integration of customized solids removal equipment (e.g. cyclone, filters) between the plasma and catalytic zones. Finally, the C_2H_4 energy cost has been considerably reduced over the years while passing

from DC (frequently used in the past), to AC and eventually to the most recent NPD power supplies.

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